



South Coast Air Quality Management District

SOx RECLAIM FINAL REPORT

WET/DRY SCRUBBING TECHNOLOGY FOR SULFURIC ACID PLANTS AND COKE CALCINER

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Executive Summary

Fine particulate matter concentrations in the Basin are among the highest measured nationwide. The Basin is classified as Non-attainment for PM_{2.5} and must meet the federal National Ambient Air Quality Standards for PM_{2.5} by 2015. Oxides of sulfur (SO_x) are a key precursor of sulfates, one of the principal components of PM_{2.5}. On average ammonium sulfate contributes approximately 30 percent of the total PM_{2.5} mass monitored in the Basin.

The SCAQMD has solicited bids for a project that involves engineering evaluations and cost estimates for installation and operation of commercially viable SO_x control technologies to further reduce SO_x emissions for seven major emitting categories of stationary source equipment in the SO_x RECLAIM program. Nexidea was awarded the study for the two Sulfuric Acid Plants and Coke Calciner in the Basin.

The results of this project will be used to assist the AQMD staff in identifying BARCT that can be potentially implemented within the 2011-2014 time frame in order to help the basin attain the PM_{2.5} air quality standards by 2014.

The first step in the evaluation was site visits to gather specific information on equipment and operating conditions, and to conduct a site-specific feasibility assessment analysis of the three facilities. The second step was to use this information to obtain preliminary designs from four technology vendors for SO₂ reduction. That information was used to determine capital and operating costs for each proposal at 5, 10 and 20 ppm SO₂ emissions. Finally, the cost effectiveness of each technology was determined. Cost effectiveness is defined as dollars of capital plus operating cost divided by tons of SO₂ reduction over a 25-year period. This Draft Final Report presents the results of these activities, and makes recommendations on BARCT levels of SO₂ emissions for the two sulfuric acid plants and one coke calciner in the SCAQMD air basin.

The results of the study show that simple caustic treating can cost effectively reduce SO₂ emissions to less than 5 ppmv for all of the units in the study; however, the recommended BARCT level is 10 ppmv due to control issues at near-zero SO₂ levels. It is recommended that Facility B Acid Plant and Facility C Calciner add a caustic scrubber to meet the 10 ppmv SO₂ level. Facility A Acid Plant already uses an SO₂-selective amine to reduce SO₂ to 20 ppmv. That unit can be revamped at low cost to meet a 10 ppmv SO₂ level, thus addition of a caustic treater to that unit is not recommended.

Executive Summary

Table 1 presents a summary of the key findings of this study. Recommended BARCT is 10 ppmv SO₂, limited by process control issues. SO₂ reduction at the 10 ppmv SO₂ level from Facility A is well under 0.1 tons per day. For Facility B, the potential reduction is 1.1 tons per day. Potential SO₂ reduction from Facility C is 1.0 tons per day. The achievable SO₂ emissions for Acid Plants is in the 0.11 – 0.14 lbs SO₂ per ton of acid produced. The achievable SO₂ emission for Coke Calciners is 0.25 lbs SO₂ per ton of coke feed.

Space appears to be readily available for Facilities A and B for upgrades to Facility A and a new wet scrubber for Facility B. Facility C has limited room for a new scrubber, but should be able to accommodate a tight design by relocating some equipment to other areas.

TABLE 1: Summary of Recommendations

Equipment	BARCT Level	Emission Reductions	Cost Effectiveness
Facilities A and B	0.14 lbs SO _x /ton acid (10 ppmv)	<0.1 tpd (A) 1.1 tpd (B)	\$1.4K - \$5.6K
Facility C	0.25 lbs SO _x /ton coke (10 ppmv)	1.0 tpd	\$2.5K - \$5.0 K

Facility and Emissions Profile

A. General Facility and Equipment Description
See Appendix for a description of each facility

B. Current Emission Profiles in 2005 and 2008
See Tables 2 and 3 below

TABLE 2: SO₂ Emissions from Sulfuric Acid Plants

Facility	Device Description	2005 Emissions (tons/day)	2006 Emissions (tons/day)	2007 Emissions (tons/day)
A	Reactor	0.04 ⁽¹⁾	0.06	0.05
B	Furnace	1.13 ⁽²⁾	1.02	0.96
		1.17	1.08	1.01

Data from Preliminary Staff Draft Report, April 3, 2008

TABLE 3: SO_x Emissions from Coke Calciner

Device ID	Rating (mmbtu/hr)	2005 Emissions (tons/day)	2006 Emissions (tons/day)	2007 Emissions (tons/day)
20	120	0.35	0.62	0.55
	Total	0.35	0.62	0.55

Note: The 2005 SO_x emissions were from SCAQMD database for the period from January 2005 – December 2005. The 2006 and 2007 emissions were reported by the facilities through a Survey Questionnaire distributed by SCAQMD in 2008.

Facility and Emissions Profile

From the site visits, the above three facilities presented the following information on current average SO₂ emissions:

Facility A Acid Plant: 20 ppmv SO₂

Facility B Acid Plant: 145 ppmv SO₂

Facility C Coke Calciner: 50 ppmv SO₂

These values match up well with the previous reported values and with the values provided by each facility; however, the potential reduction in SO₂ from Facility C based on the 50 ppmv level is higher than reported by Facility C in Table 3 above. This suggests that the 50 ppmv average SO₂ emission level may be too high, and this study may overstate the potential emission reduction from Facility C.

Control Technology – Feasibility Analysis

A. Critique on SCAQMD Preliminary Draft Staff Report

In Section 6.2 on Sulfuric Acid Plants, the information for emissions control system for Facility B is incorrect for the plant currently in operation (Plant 4). The report states that the Acid Plant has a packed-bed scrubber, mist eliminator and flare. Plant 4 has none of these controls. It is a conventional double-absorption plant, with tail gas from the second absorber going directly to a stack for discharge. This report will confirm the Draft Staff Report conclusion that an SO₂ emission rate of 0.2 lb/ton acid, or lower, can be achieved with wet scrubbing of Acid Plant tail gas before discharge.

The information on Facility C coke calciner is in agreement with the information supplied by the facility. The conclusion that wet scrubbing can further reduce SO₂ emissions is born out by this current study.

B. Literature Research on Control Technology

Wet scrubbing of gas streams with basic solutions to remove acid gases has been practiced worldwide for many decades. It is one of the most simple of all treating technologies for reducing sulfur, both in its reduced (H₂S) and oxidized (SO₂ and SO₃=) form. All refineries practice wet gas scrubbing to remove H₂S from various refinery gas streams, using one of several types of amine solutions. Power plants use lime, limestone and ammonia to reduce SO₂ in flue gas streams. For small gas flows, where very low SO₂ levels are desired, caustic (NaOH) or soda ash (Na₂CO₃) are often used. While numerous technology vendors offer wet scrubbing for SO_x reduction and have their own proprietary designs and equipment, this is an open-art technology that almost any gas treating consultant or engineering firm can design and engineer.

The three vendors contacted for this study that use a non-regenerable reagent are some of the best in the gas treating business. All three recommend the use of caustic as the reagent for treating the gas streams from the acid plants and calciner to achieve very low levels of SO₂. One vendor uses a proprietary SO₂-selective amine to achieve very low levels of SO₂, without the need for constant makeup and purge of reagent.

C. Identification of Relevant Vendors and Contact Status

The SCAQMD is familiar with four technology vendors that can supply technologies to reduce SO₂ emissions from Sulfuric Acid Plants and Coke Calciners. These companies are:

Control Technology – Feasibility Analysis

- 1) Cansolv Technologies, Inc (CTI)
- 2) Monsanto Envirochem Systems (MECS)
- 3) Belco Technologies
- 4) Tri-Mer

All four companies were sent requests for basic sizing and cost information for gas treating facilities that can reduce SO₂ emissions. Each was asked to supply designs to meet 5,10 and 20 ppmv SO₂ in the treated gas streams. Belco, Tri-Mer and MECS responded with proposals. Cansolv Technologies responded with a letter stating that their technology is not economically attractive as a polishing unit, and they will not bid on Facility B or coke calciner. They will support the necessary upgrades to Facility A's Cansolv Unit to allow it to meet a 10-ppmv SO₂ level.

D. Discussion on Control Technology and Potential Emissions Reductions

In general there are two designs for Sulfuric Acid Plants – Single and Double Absorption. The terms refer to the number of acid absorption towers used to capture SO₃= and convert it to sulfuric acid. Older plants are usually single absorption. Due to the limits on conversion equilibrium with single absorption plants, unconverted SO₂ in the tail gas from the Acid Plant is in the 2000 – 3000 ppmv range. Some form of SO₂ capture is definitely required for this level of emissions.

Double absorption plants improve SO₂ conversion by placing the first of two acid absorption towers after the third converter catalyst bed. This first tower absorbs most of the SO₃= before the gas goes to the fourth catalyst bed. A second acid absorption tower follows the fourth catalyst bed. Because most of the SO₃= from the first three beds has been removed in the first acid absorption tower, the equilibrium conversion of the remaining SO₂ to SO₃= is improved in the fourth bed. The second acid absorber tower then removes most of the remaining SO₃=. Overall conversion is typically 98 – 99%, and tail gas SO₂ is typically 100 – 200 ppmv. Historically double absorption plants have needed no further SO₂ reduction before the tail gas is emitted to the atmosphere, hence, revamping of single absorption plants to double absorption has been an accepted method of upgrading older plants to meet current SO_x limits.

Control Technology – Feasibility Analysis

Cesium catalyst can be used with, or in place of, the normal vanadium pentoxide catalyst in the SO₂ converter. Used in the first catalyst bed of a single absorption unit, it can help improve overall conversion. Used in the fourth bed of a double absorption plant, it can improve the equilibrium conversion of SO₂ by about 30% and thus reduce SO_x emissions by this amount.

Facility A acid plant is of the older single absorption design. It originally had a Monsanto-designed ammonium sulfate (“Ammsox”) tail gas unit to reduce SO₂ emissions to the 300-350 ppmv range. This treating unit was replaced in 2001 with a Cansolv amine SO₂ wet scrubber. Details of this design and operation are presented in the Appendix.

Facility B has a newer acid plant with double absorption technology. This plant has no treating of the Acid Plant tail gas. Details of the design and operation can be found in the Appendix.

Wet and dry scrubbing are used very often to reduce SO_x in gas streams as diverse as power plants, ore smelters, paper plants, various refinery units, acid plants and coke calciners. For Sulfuric Acid Plants, the plant design that lends itself best to SO_x reduction is wet scrubbing. Some power plants use dry scrubbing to reduce SO₂. This technology works well for the coke calcining process, and is used at Facility C coke calciner.

Dry scrubbing for a process unit like a Calciner would most likely use a spray dry absorber (SDA). Dry lime (CaO) is mixed with enough water to make it pumpable, then sprayed into the hot flue gas stream from the afterburner. The calcium hydroxide form of the lime, Ca(OH)₂, reacts with SO₂ to make calcium sulfate. The calcium sulfate, unreacted lime and any remaining coke fines are removed in a bag house for disposal. Even for a small removal of SO₂, the amount of solids from the SDA unit is considerable, and can be difficult to dispose. Removal of SO₂ with an SDA unit is typically in the 97 – 98% range. Overfeeding lime can increase SO₂ removal to the 99% range.

Wet scrubbing can be divided into two broad categories: (1) Those that use non-regenerable chemical absorbents and (2) those that use regenerable solvents. The non-regenerable units typically use caustic (NaOH) or soda ash (Na₂CO₃) as the absorbent. Large power plants typically use limestone (CaCO₃) to capture SO_x; however, this type of

Control Technology – Feasibility Analysis

wet scrubber generates large amounts of calcium sulfate (CaSO_4), which must be dewatered in large evaporation ponds, totally unsuited for refineries or chemical plants. For Sulfuric Acid Plants or Calciners, the usual chemical absorbent is NaOH. Once-through scrubbing requires the least amount of equipment, but NaOH must be added to the scrubber continuously. In plants with high SO₂ removal levels, this cost can be prohibitive.

Regenerable solvents, such as SO₂-selective amines, require more equipment and energy, but save on operating costs since the solvent is reused continuously. Since the capital cost of a regenerable unit is about the same regardless of feed SO₂ concentration, the cost effectiveness of regenerable systems increases with feed SO₂ concentration. The economic breakeven point for using regenerable amines is around 200 – 250 ppmv of inlet SO₂. Thus, a regenerable amine scrubber would be most applicable on a single absorption Acid Plant where inlet SO₂ concentrations to the absorber are in the 2000 – 4000 ppmv range, or on a Calcliner that has no pretreatment of SO₂. Regenerable units are not typically specified or chosen as polishing units. One limitation of the regenerable units is disposal of the pure SO₂ product from the amine regeneration tower. SO₂ gas can be compressed to liquid SO₂. It can be converted easily to sulfuric acid or to elemental sulfur if a Claus Unit is located nearby. If these options are not available to the Acid Plant, this technology cannot be used.

Either regenerable or non-regenerable SO₂ absorption technologies can be effective in reducing SO_x emissions down to 10 ppmv or less in Sulfuric Acid Plants, but a regenerable amine would only get to this level on Calciners if the absorber inlet gas can be cooled sufficiently.

Waste disposal is always an issue in neutralizing acidic materials such as SO₂. If once-through chemical absorbents are used, there will be sodium sulfite (Na_2SO_3) or sodium sulfate (Na_2SO_4) salts to dispose. Depending on limits on wastewater treating, this may be an issue. Typically any effluent sulfite streams must be oxidized to sulfates to eliminate chemical oxygen demand. Regenerable solvents produce a small amount of waste sodium sulfate salts from the heat stable salt removal system used to keep the solvent free of acids.

For the small amount of effluent water and sodium salts produced from the designs in this study, the impact on effluent treating systems should be small; however, each facility must determine how the application of wet scrubbing will affect its specific permit limits.

Cost Analysis

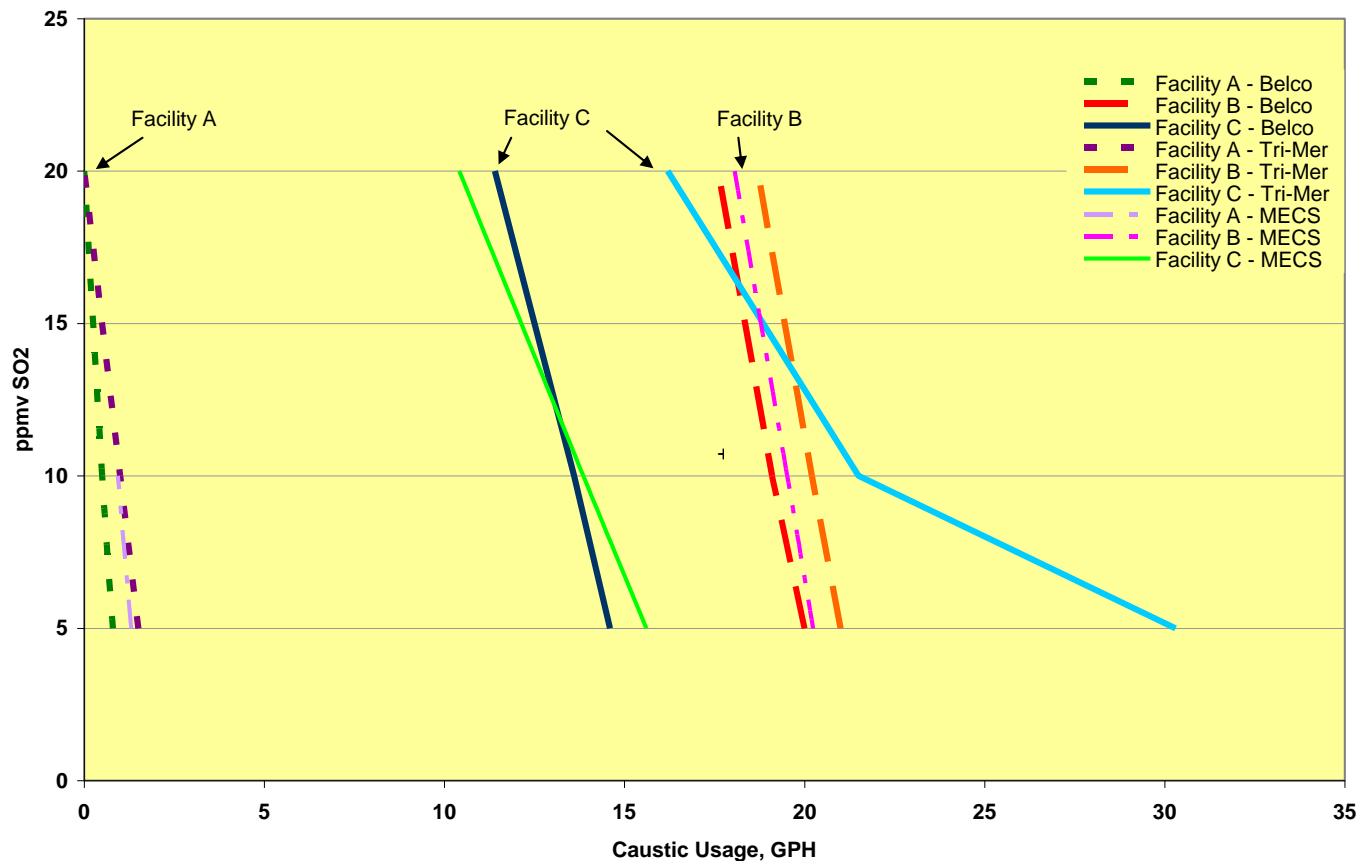
A. BARCT Levels

Both Sulfuric Acid Plants and the Coke Calciner start with relatively low levels of SO₂ in the current discharge streams: 20 to 145 ppmv. Treating down to 10 ppmv SO₂ is easy and straightforward with caustic treating. Belco, Tri-Mer and MECS all state that they can provide designs that will achieve SO₂ levels down to 1-2 ppmv with caustic treating for Facilities B and C. Cansolv can achieve 10 ppmv SO₂ with minor upgrades to the Facility A Acid Plant, and believe that 5 ppmv is possible if all process variables are carefully controlled.

The recommended treat level is 10 ppmv for all three facilities. The reason for this slightly higher value is that treating to 5 ppmv is essentially treating to zero. At this extremely low level, control over caustic injection becomes difficult. Refer to Figure 1, which shows caustic addition versus SO₂ in the treated gas. Note that the caustic injection rate is given in gallons per hour. A very small change in caustic addition rate has a large impact on SO₂ level. Even if the caustic is diluted to 20%, the injection rate is still very small, and normal load changes in the units can make constant control difficult. Belco warns that control at <5 ppmv requires an increase in the pH of the caustic solution. As the pH rises, the tendency towards scaling the absorber tower and its internals increases, and the composition of makeup water to the unit must be carefully watched. If the pH is raised too high, it is possible to start absorbing CO₂, which can produce a hard, insoluble sodium carbonate scale in the tower. Control at <5 ppmv almost certainly will result in over-injection of caustic, which is both wasteful and adds to the treating load in the effluent treatment plant. Control at 10 ppmv gives the operator more control room to respond to plant load changes without undue attention to the unit.

Cost Analysis

Figure 1: Treated Gas SO₂ versus Caustic Usage



Tri-Mer's caustic usage for the Calciner at 5 ppmv SO₂ appears to be an erroneous value. Tri-Mer has been asked to verify this value, but has not yet responded.

B. Approach and Basis for Cost Estimates

Facility A Acid Plant uses a regenerable solvent for reducing tail gas SO₂ emissions. Current emissions are in the 20 - 30 ppmv range. With some minor modifications it is felt that this unit can achieve 10 ppmv SO₂ emissions, thus no further wet scrubbing technologies would be required.

Facility B Acid Plant has emissions of around 150 ppmv, or 1.7 lb SO₂ / lb acid produced. Inlet SO₂ emissions of 150 – 200 ppmv are too low to justify a regenerable amine. A caustic polishing scrubber is the best solution to meeting 10 ppmv SO₂ emissions.

Cost Analysis

Facility C Calciner has a highly effective dry SOx removal system in current operation. A caustic polishing scrubber is the most effective way to achieve 10 ppmv SO₂.

C. Approach and Basis for Equipment Sizing

Information needed by the technology vendors to size the requested units is presented in the appendices.

D. Equipment Cost Information

Capital cost information is given in the Appendices. Belco and Tri-Mer supplied costs for inside battery limit (ISBL) equipment only. MECS supplied cost estimates for total installed equipment (TIC). All vendor capital costs were done on a U.S. Gulf Coast (USGC) basis as is typical. A 20% location factor was added to cover the difference in labor costs between the USGC and the Los Angeles area.

A local cost estimator supplied estimates to take the vendors' estimates to the fully installed level of detail. Those costs are broken down into the usual labor, materials and subcontract categories. They include the details on site work, concrete, structural steel, equipment, piping, instrumentation, electrical and painting.

It must be pointed out that little time was spent in each facility, and little information was available on issues such as equipment relocation needed to make room for the new scrubbers; utility upgrades that might be required to supply power and water; and possible upgrades to effluent treating systems to handle the extra water and sodium salts produced in the scrubbing processes. To handle these unknowns, a 35% contingency was added to the base costs. Owner's costs were not included.

Cost estimates are felt to be "good ballpark" numbers, typical of what other facilities of this type would cost in this location, but are not of the quality for use in justifying projects to company management. Much more time and detailed information would be required to reach that level of accuracy.

Summary sheets for each estimate are given in the Appendices.

Cost Analysis

E. Annual Operating Costs

Annual operating cost information is given in the Appendices. These are the costs based on information supplied by the vendors for their proposed systems.

F. Cost Effectiveness Analysis

The methodology used to determine the relative effectiveness of the proposed technologies is the Cost Effectiveness ratio. This is the ratio of the Present Worth Value of the capital and annual operating costs for each technology divided by the tons of SO₂ reduced for the period. The calculation is as follows:

$$PWV = C + (CF \times A)$$

Where:

PWV = Present Worth Value, \$

C = Capital cost of the proposed treating unit, \$

CF = Conversion value from Annual Cost to Present Worth Value, a fixed value

A = Annual operating costs for the unit, \$/year

Assumptions:

There are no annual savings to be gained from operating a wet scrubbing unit

There are no replacements to the units over their lifetime

The SO₂ reduction period is assumed to be 25 years

The interest rate in the PV calculations is 4%

The Cost Effectiveness ratio is calculated as:

$$CE = \frac{PWV}{E}$$

Where:

CE = Cost Effectiveness, \$/ton SO₂ reduced

PWV = Present Worth Value

E = Tons of SO₂ reduced over a 25 year period

Cost Analysis

The total installed equipment costs for the Belco, Tri-Mer and MECS proposals are presented in Table 1. Estimates for the Cansolv upgrades were provided by the Consultant, who has knowledge of the Cansolv Unit.

Table 1: Estimated Installed Equipment Costs

	Facility A	Facility B	Facility C
Belco	\$3,090,131	\$6,579,231	\$13,302,633
Trimer	\$2,999,249	\$13,316,664	\$21,059,914
MECS	\$4,043,137	\$7,497,015	\$16,826,926
Cansolv	\$500,000		

The low estimated cost for Facility A's unit reflects the belief that the existing unit can be easily upgraded to meet the proposed 10 ppmv SO₂ limit. Very little new or modified equipment would be required for this upgrade. Details of the estimate for upgrading the unit are presented in the Appendix. Details of the cost estimates for Facilities B and C are also presented in the Appendix.

G. Cost Effectiveness Values

Table 2 presents the Cost Effectiveness Values for each case evaluated. The cases were as follows:

- Scrubbers for three facilities were evaluated: Facility A, Facility B, and Facility C
- Four technologies, Belco, Tri-Mer, MECS and Cansolv were evaluated
- Each technology was evaluated at 5, 10 and 20 ppmv treated gas SO₂ emissions

Cost Analysis

Table 2: Cost Effectiveness

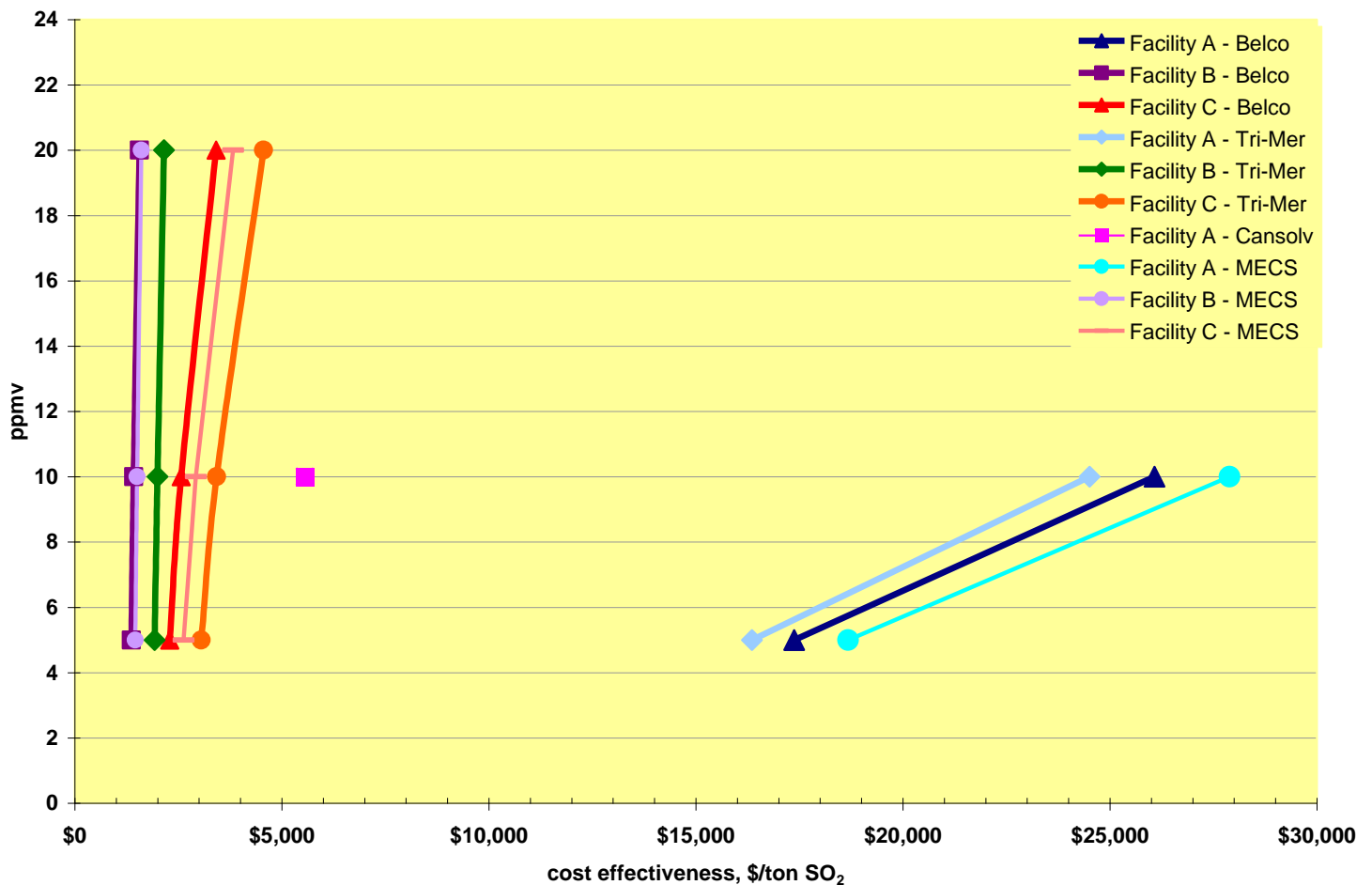
	<u>Cansolv</u>	<u>Tri-Mer</u>	<u>Belco</u>	<u>MECS</u>
Facility A @ 5 ppm	NA	\$16,682	\$17,596	\$18,675
Facility A @ 10 ppm	\$5,556	\$24,906	\$26,273	\$27,892
Facility A @ 20 ppm	NA	NA	NA	NA
Facility B @ 5 ppm	NA	\$2,158	\$1,594	\$1,458
Facility B @ 10 ppm	NA	\$2,229	\$1,644	\$1,503
Facility B @ 20 ppm	NA	\$2,388	\$1,757	\$1,605
Facility C @ 5 ppm	NA	\$3,375	\$2,469	\$2,624
Facility C @ 10 ppm	NA	\$3,768	\$2,749	\$2,923
Facility C @ 20 ppm	NA	\$4,946	\$3,589	\$3,821

Figure 2 presents achievable levels of SO₂ emissions versus Cost Effectiveness of each technology for each facility. As can be seen from Figure 2 and the table above, the Cost Effectiveness of the Belco, Tri-Mer and MECS technologies is close together for each facility. In fact, the numbers are so close for each case that it is not possible to distinguish between them at this level of cost estimating. What the table and figure indicate is that all the technologies are cost effective over a 25-year period, with all CE values for Facilities B and C less than \$5,000/ton.

For Facility A, the low inlet SO₂ level shows its impact on Cost Effectiveness. Belco, Tri-Mer and MECS have similar CE ratios, varying between about \$17,000 and \$28,000/ton SO₂ at SO₂ levels between 5 and 10 ppmv. This has more to do with the few tons/year of reductions than with capital or operating cost. There simply isn't that much CO₂ to reduce when the starting level is already at 20 ppmv. The single point for the Cansolv technology shows the Cost Effectiveness of reducing SO₂ from 20 ppmv to 10 ppmv by modifying the existing plant. The curve shows that it is far more cost effective to improve the existing Cansolv operation than to add a new caustic scrubber system.

Cost Analysis

Figure 2: Cost Effectiveness Versus SO₂ in Treated Gas



H. Project Timing

The key elements of a project using any of the above technologies are:

- Process Engineering (Vendor and Facility)
- Detailed Design (Engineering Company and Facility)
- Procurement (Engineering Company and/or Facility)
- Construction (Construction Company usually)
- Permitting (Facility and AQMD)

For the technologies that require new scrubbing facilities, the estimated project time is 24-30 months. It is assumed that permitting

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activities will run parallel to process and detailed design work. For the Cansolv revamp work, the estimated project time is 12 months since there is little new or long-lead equipment involved, and the process design should be simple. The need to do certain construction work during major maintenance turnarounds can extend project completion time. In none of the cases considered here should total project time exceed 36 months.

I. Conclusions

Emissions of SO₂ from the two Sulfuric Acid Plants and the Calciner can be reduced to levels <5 ppm in a cost-effective manner. The recommend SO₂ target level is 10 ppmv due to control issues at levels less than 5 ppmv. Control at <5 ppmv SO₂ can lead to potential absorber tower fouling problems and wasted caustic.

Caustic polishing is recommended for Facility B's Acid Plant and the Facility C Calciner. A revamp of the existing Cansolv Unit is recommended for Facility A's Acid Plant.

The tons per day emission reductions are estimated to be in Table 3.

Table 3: Estimated Emissions Reductions

TPD SO ₂ Reduction	-
Facility A @ 5 ppm	0.050
Facility A @ 10 ppm	0.033
Facility A @ 20 ppm	NA
Facility B @ 5 ppm	1.192
Facility B @ 10 ppm	1.149
Facility B @ 20 ppm	1.064
Facility C @ 5 ppm	1.122
Facility C @ 10 ppm	0.997
Facility C @ 20 ppm	0.748